Fabrication of robust MOFs/aerogel composite via covalent post-assembly method

Yue Xu, a Xu Zhai, a Xuan-He Wang, a Lin-Lin Li, a Huan Chen, a Fu-Qiang Fan, a
Xiao-Jue Bai, a Jun-Yi Chen, b and Yu Fu*a

a Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, P. R. China
b College of Life Science, Tarim University, Alaer 843300, P. R. China.
Experimental Section

Materials

All chemicals used in this work were analytical grade and without further purification. Zirconium chloride (ZrCl₄), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), imidazole-2-carboxaldehyde, 2-aminoterephthalic acid (H₂BDC-NH₂), terephthalic acid (H₂BDC), pyromellitic dianhydride (PMDA), 4, 4’-oxydianiline (ODA), N, N-dimethyacetamide (DMAC), triethylamine, tetrabutylammonium bromide (TBAB), (R)-styreneoxide, polyvinylpyrrolidone (PVP), 1-bromo-2, 3-epoxypropane and 1, 2-epoxyhexane were purchased from Energy Chemical (Shanghai). N, N-dimethylformamide (DMF), ethanol (C₂H₅OH) and acetic acid glacial (CH₃COOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Methylene blue were purchased from Kermel (Tianjin). The water used in this work was deionized water.

Synthesis of UiO-66

Zirconium (IV) chloride (105 mg, 0.45 mmol) and terephthalic acid (74.8 mg, 0.45 mmol) were dissolved in 15 mL DMF with 2.08 mL glacial acetic acid in a 20 mL vial with Teflon-lined cap. The vial was then placed in a 120°C oven for 24 h. After cooling to ambient temperature, the particles were collected by centrifugation (fixed-angle rotor, 7000 rpm, 5 min), followed by washing with 5×10 mL MeOH. The particles were then soaked in CH₂Cl₂ for 3 days with solvent changed daily, before being dried under vacuum at room temperature.

Synthesis of UiO-66-NH₂
Zirconium (IV) chloride (105 mg, 0.45 mmol) and 2-aminoterephthalic acid (81.6 mg, 0.45 mmol) were dissolved in 15 mL DMF with 2.08 mL glacial acetic acid in a 20mL vial with Teflon-lined cap. The vial was then placed in a 120°C oven for 24 h. After cooling to ambient temperature, the particles were collected by centrifugation (fixed-angle rotor, 7000 rpm, 5 min), followed by washing with 5×10 mL MeOH. The particles were then soaked in CH₂Cl₂ for 3 days with solvent changed daily, before being dried under vacuum at room temperature.¹

**Synthesis of ZIF-90**

In the preparation of ZIF-90, we adopted and improved the method of Fa-Kuen Shieh’s research group (a typical H₂O/ alcohol/ PVP system). Zinc nitrate (371.25 mg) was added to 12.5 mL mixed solution of the selected alcohol (6.25 mL, i.e., ethanol, propan-2-ol, isobutanol, and tert-butanol) and deionized (DI) water (6.25 mL) in which the selected alcohol was as a triggered solvent, and was subsequently added to the above-mentioned mixed solvent (12.5 mL) with ICA (480 mg) and PVP (500 mg). After mixing, the resulting powder was stirred for a few minutes. All reactions were carried out at room temperature. Finally, the as-obtained products were collected by centrifugation (11000 rpm), washed with excess methanol, and vacuum dried at 50°C.²

**Synthesis of UiO-66-NH-PMDA**

200 mg of dried UiO-66-NH₂ powder was fully dispersed into 22.5 mL DMAC with the assistance of ultrasound, and the excess PMDA was added. The suspension was stirred in an ice bath for 96 h, which whole process takes place under the
protection of nitrogen. Then the reaction mixture was centrifuged for separation. The powder was washed with MeOH for 5 times. Finally, the particles were then soaked in CH₂Cl₂ for 3 days with solvent changed daily, before being dried under vacuum at room temperature.

**Synthesis of ZIF-90-ODA**

200 mg of dried ZIF-90 powder was fully dispersed into 22.5 mL DMAc with the assistance of ultrasound, and the excess ODA was added. The suspension was heated and stirred in an oil bath (100°C) for 8h, which whole process takes place under the protection of nitrogen. Then the reaction mixture was centrifuged for separation. The powder was washed with MeOH for 5 times. Finally, the particles were then soaked in CH₂Cl₂ for 3 days with solvent changed daily, before being dried under vacuum at room temperature.

**Synthesis of PI**

ODA and DMAC were added into a 25 mL schlenck flask fitted with a mechanical stirrer. Once ODA had dissolved completely, half equivalent molar quantity of PMDA was added, and the mixture was stirred for 4 h. And the remaining PMDA was added in two separate increments. The whole process was in a nitrogen atmosphere. Then a polymer (amic acid) (PAA) solution with a solid content of about 12 wt.% was obtained after continued stirring of the reaction mixture overnight. Then, the resultant solution was poured into cool deionized water and deposited. After washing, freeze drying and crushing, PAA powder was obtained. The ammonium salt solution of PAA was prepared from PAA (84 mg) and triethylamine (TEA, 60 μL) in deionized water.
(5 mL) (solid content of 1.8%). Afterward, the resulting suspensions were transferred to 5 mL cylindrical Teflon vials, frozen in a laboratory freezer, and dried in a Christ freeze-dryer. After 24–36 h in the lyophilizer, the samples were removed and heated at gradient temperatures of 150°C for 0.5 h, 250°C for 0.5 h and 300°C for 1 h to induce thermal-imidization to obtain the PI aerogel.³


The preparation of the composite materials was roughly similar to the method of preparing pure PI. But first UiO-66-NH-PMDA/UiO-66 and ODA should be evenly dispersed into DMAC, and then PMDA should be added under the protection of nitrogen. The amount of PMDA should be slightly expanded accordingly. For the ZIF-90 system, since which is modified by ODA, it is equivalent to the introduction of amino group. The amount of PMDA should also be expanded accordingly. Then other experimental steps were the same as that of preparing PI.

**Characterization**

Morphologies of samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010) and transmission electron microscopy (TEM, JEOL JEM-2100F). The crystal structure of the product was tested by X-ray diffraction (XRD) on PANalytical Empyrean X-ray diffractometer with Cu Kα1 (λ = 1.5406 Å) radiation. The organic groups in PI aerogel and hybrid aerogel and MOFs were characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70). The Zirconium ion contents in the dye aqueous solution after adsorption was determined by inductively coupled plasma emission spectrometry.
(ICP-OES, PE Optima 8300). Thermogravimetric analysis (TGA) was carried out with a thermobalance (TGA-2050, TA Instruments) under N₂ from room temperature to 800°C with a temperature ramp of 10°C/min. Hydrophilicity and hydrophobicity of the materials were tested by Standard contact angle (SCA) meter (KRUSS-DSA25). The freezer dryer was manufactured by Biocool Instrument Co., Ltd.

**Absorption**

Adsorption kinetics were studied by soaking the UiO-66-PI or UiO-66-NH₂ nanoparticles in 10 mL of aqueous solution containing the contaminant (5 mg/L Methylene Blue) for one day. The absorbancy change of known dye solution at different time points was analyzed by UV-vis to determine the concentration based on a calibration curve prepared from solutions with known contaminant concentrations. The Absorption spectra from 200 to 800 nm were measured with an optics spectrometer (Ocean Optics, Maya 2000PRO). Fig. 2c, d shows the adsorbed quantity, qt, of MB dye on UiO-66-PI and UiO-66-NH₂ as a function of time t, in which q₀ and qₑ were calculated using the following relationship:

\[
q_t = (C_0 - C_t) \times \frac{V}{m}
\]

\[
q_e = (C_0 - C_e) \times \frac{V}{m}
\]

Where \( q_e \) (mg·g⁻¹) is the amount of dye adsorbed onto the adsorbent at equilibrium and \( q_t \) stands for that at time \( t \), with \( C_0 \), \( C_e \) and \( C_t \) (mg/L) denoting the liquid-phase concentrations of dye at initial, equilibrium and time \( t \), and \( V \) (L) and \( M \) (g) as the volume of dye solution and the mass of adsorbent, respectively.

\[
t/q_t = 1/((k_2 \times q_e^2) + t/q_e)
\]
Where $q_t$ and $q_e$ were the adsorption capacities at time $t$ and equilibrium respectively, and $k_2$ was the rate constant of the pseudo-second-order model (h·g·mg$^{-1}$).4-6

**CO$_2$ cycloaddition reaction catalyzed by UiO-66-PI and UiO-66-NH$_2$ nanoparticles powder catalyst**

The UiO-66-PI (10 wt.%) and UiO-66-NH$_2$ nanoparticles powder were vacuum-dried at 100°C for 10 h before use. The catalytic reaction was typically conducted in a schlenck tube containing epoxides (about 4 mmol) and with a CO$_2$ balloon at a pressure of 1 atm in a solvent-free environment. The added catalysts were 0.5 mol% (about 6 mg UiO-66-NH$_2$ powder, about 60 mg UiO-66-PI 10 wt.%) with a cocatalyst of TBAB (64 mg, 5 mol%). The reaction temperature and reaction time are all 80°C and 18 h. The products were analyzed by gas chromatography (GC, SP-3420A, Beijing Beifen-Ruili Analytical Instrument Co., Ltd.) equipped with a flame ionization detector.6
**Fig. S1** SEM images of UiO-66-NH$_2$ and UiO-66-NH-PMDA.
Fig. S2 XRD patterns of UiO-66-NH$_2$ and UiO-66-NH-PMDA compared to UiO-66-NH$_2$ simulation.
**Fig. S3** Photographs of UiO-66-PI with different MOF contents (0 wt.% / 2 wt.% / 10 wt.% / 20 wt.%) (up). The low density of UiO-66-PI (down).
Fig. S4 SEM image of UiO-66-NH₂ nanoparticles in UiO-66-PI.
Fig. S5 SEM image of UiO-66-PI aerogel with 2 wt.% UiO-66-NH$_2$. 
Fig. S6 TEM images of UiO-66-NH$_2$ nanoparticles in UiO-66-PI.
Fig. S7 FT-IR spectrum of UiO-66-PI with 2 wt.% and 10 wt.% UiO-66-NH₂.
Fig. S8 TGA curves of (a) PI aerogel. (b) UiO-66-PI (10 wt.%); (c) UiO-66-PI (20 wt.%). (d) UiO-66-NH$_2$ nanoparticles in air atmosphere.
**Fig. S9** $\text{N}_2$ adsorption/desorption curve of UiO-66-PI and the corresponding micropore distribution.
**Fig. S10** Photograph of UiO-66-PAA (using bare UiO-66 substituting for functionalized UiO-66-NH$_2$).
Fig. S11 Schematic diagram of the preparation of ZIF-90-PI aerogel via covalent post-assembly Method.
Fig. S12 (a) SEM image of ZIF-90 nanoparticles. (b-c) SEM images of ZIF-90-ODA-PI. (d) TEM image of ZIF-90-ODA-PI. (e) photograph of ZIF-90-ODA-PI. (f) XRD patterns of ZIF-90 and ZIF-90-ODA-PI.
Fig. S13 Zeta potential distribution of UiO-66-NH$_2$. 
**Fig. S14** Time evolution of the UV-vis spectra collected in different time during the adsorption of MB on PI aerogel.
**Fig. S15** Photographs after different time (0 h/ 3 h/ 6 h/ 24 h) during the adsorption of MB on UiO-66-PI aerogel.
**Fig. S16** Plot of the pseudo-first-order kinetic model for MB absorption on UiO-66-PI and UiO-66-NH$_2$. 
Fig. S17 XRD patterns of the UiO-66-PI composite after cyclic tests in dye adsorption.
Table S1 The removal rates of dye on UiO-66-PI (20 wt.%) and UiO-66-NH$_2$ powder.

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<th>Types of dye</th>
<th>Removal rate (%)</th>
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<tr>
<td></td>
<td>MOF-PI aerogel</td>
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<td>MB</td>
<td>98.2</td>
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Table S2 Kinetic parameters for the adsorption of MB on UiO-66-PI (20 wt.%) and UiO-66-NH$_2$ powder.

<table>
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<th>Kinetic parameters</th>
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<tr>
<td></td>
<td>$q_{\text{e,cal}}$ (mg·g$^{-1}$)</td>
<td>$k_2$ (mg·g$^{-1}$·h$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>UiO-66-PI</td>
<td>3.70</td>
<td>0.278</td>
<td>0.9879</td>
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<tr>
<td>UiO-66-NH$_2$ powder</td>
<td>3.21</td>
<td>0.291</td>
<td>0.9979</td>
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Table S3 Zr concentration detected by ICP-OES on pure water and water after treatment with UiO-66-PI (20 wt.%).

<table>
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<th>Zr concentration (ppm)</th>
<th>Pure water</th>
<th>Aqueous solution containing MB after absorption by hybrid aerogel</th>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
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Aqueous solution was obtained after soaking with UiO-66-PI (20 wt.%) for 24 h.

References:

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<th>Substrate</th>
<th>Catalyst</th>
<th>Product</th>
<th>Yield (%)</th>
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<tr>
<td></td>
<td>UiO-66-NH₂</td>
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<td>80.63</td>
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<tr>
<td></td>
<td>UiO-66-PI</td>
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<td>80.45</td>
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<tr>
<td></td>
<td>UiO-66-NH₂</td>
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<td>51.82</td>
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<tr>
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<td>UiO-66-PI</td>
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<td>UiO-66-NH₂</td>
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<tr>
<td></td>
<td>UiO-66-PI</td>
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<td>66.34</td>
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Table S4 Yield for cyclic carbonates catalysed by UiO-66-NH₂ and UiO-66-PI.